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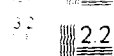
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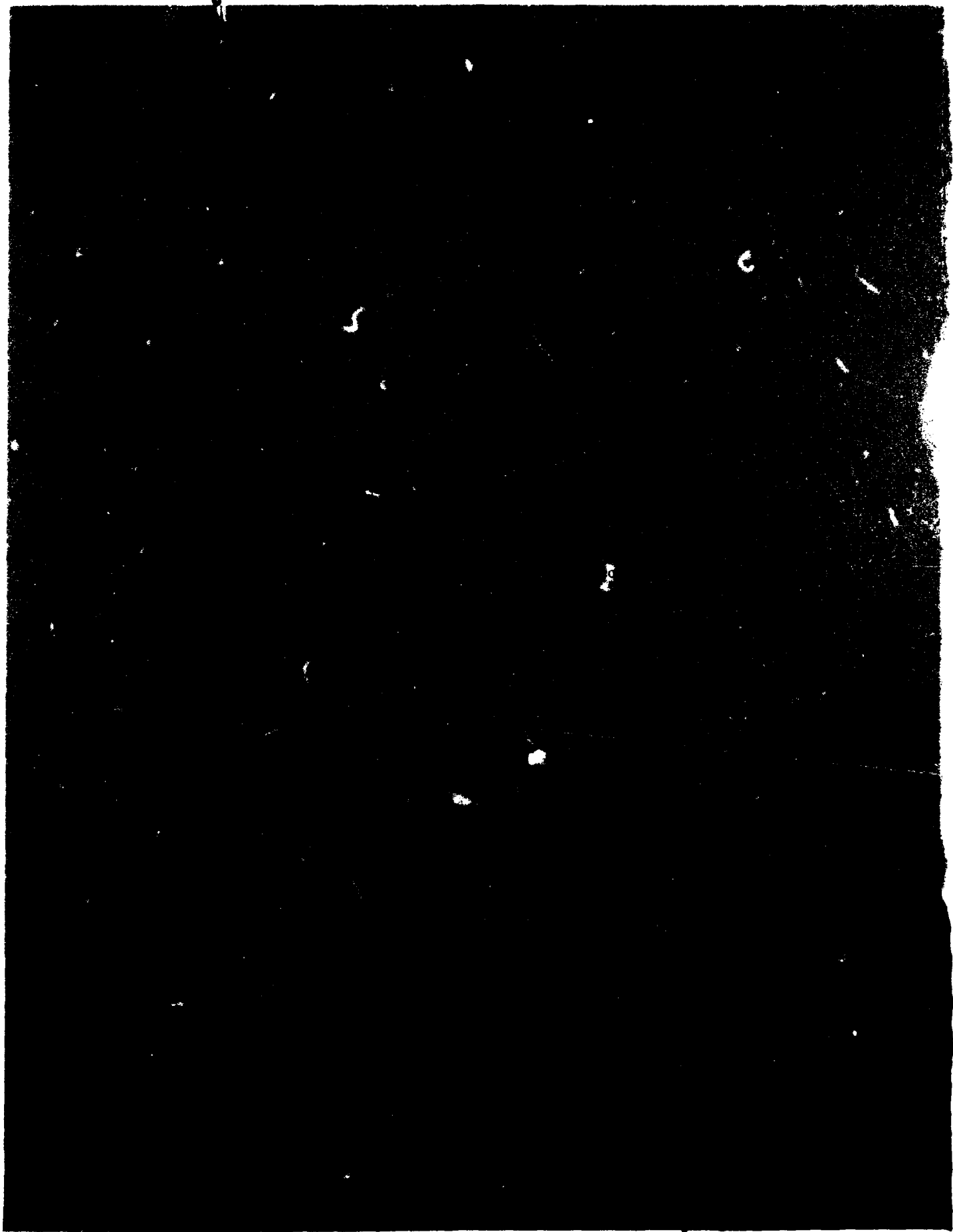


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CONTENTS

	<u>Page</u>
1. INTRODUCTION	5
2. THEORY	6
3. DISCUSSION OF AND APPROXIMATIONS TO $\Delta_n(r,R)$	11
4. ESTIMATION OF γ and R	16
5. CONCLUSION	19
LITERATURE CITED	20
DISTRIBUTION	29

APPENDICES

A.--CALCULATION OF $\lambda_2(n)$ AND $\lambda_4(n)$	21
B.--FUNCTIONS $\Delta_n(0,y)$, $\Delta'_n(0,y)$, AND $\Delta''_n(0,y)$	25

FIGURES

1. Function $\Delta_n(0,y)$ for $n = 2, 4$, and 6 versus y	17
2. Function $\Delta'_n(0,y)$ for $n = 2, 4$, and 6 versus y	18
3. Function $\Delta''_n(0,y)$ for $n = 2, 4$, and 6 versus y	18

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1. INTRODUCTION

An earlier report¹ attempts to reconcile the multipolar lattice sums, A_{nm} , of various structures to the phenomenological crystal field parameters, B_{nm} , for a number of rare-earth ions. In the theory that was used, three parameters were introduced. For calcium tungstate, the three parameters introduced were r , the outward expansion of the radial wave functions from the Hartree-Fock value; q , the effective charge on the oxygen ion; and η , an effective position of the oxygen with respect to the tungsten site chosen such as to reproduce the lowest of the $(WO_4)^{-2}$ complex when viewed from a distance large compared with the W-O distance. This model, when used with appropriate shielding factors,²⁻⁵ gave excellent results for calcium tungstate. Later improvements⁶ in the three-parameter theory gave better results for calcium tungstate. For other host materials such as YVO_4 , the same procedure does not give satisfactory results.

Therefore, it was decided to investigate the possibility of a correction due to the penetration of the rare-earth electrons into the charge distribution on the ligands. The exchange of rare-earth electrons with the electrons on the ligands was ignored in the investi-

¹Richard P. Leavitt, Clyde A. Morrison, and Donald E. Wortman, *Rare Earth Ion-Host Crystal Interactions*, 3. Three-Parameter Theory of Crystal Fields, Harry Diamond Laboratories HDL-TR-1673 (June 1975).

²R. M. Sternheimer, *Phys. Rev.*, **84** (1951), 244.

³R. E. Watson and A. J. Freeman, *Phys. Rev.*, **135** (1964), A1209.

⁴D. Sengupta and J. O. Artman, *Phys. Rev.*, **B1** (1970), 2986.

⁵P. Erdős and J. H. Kang, *Phys. Rev.*, **B6** (1972), 3393.

⁶Clyde A. Morrison, Nick Karayianis, and Donald E. Wortman, *Rare-Earth Ion-Host Lattice Interactions*, 4. Predicting Spectra and Intensities of Lanthanides in Crystals, Harry Diamond Laboratories HDL-TR-1816 (June 1977).

gation. The effects of charge penetration were previously calculated,⁷ but the method followed did not leave any parameters that could be used to fit the experimental data; thus, this method is not suitable for our purposes.

2. THEORY

The charge distribution, $\rho(r_1)$, surrounding the ligand ion is chosen to be spherically symmetric and of the form

$$\rho(r_1) = N r_1^2 e^{-\gamma r_1}, \quad (1)$$

where $N = \gamma^5 Q / 96\pi$ and Q is the effective charge on the ligand. Such a charge density is expected for hydrogenic wave functions representing the six 2p electrons or for both the 2s and 2p electrons using five Slater-type orbitals.⁸

We let \vec{R} be the position of the nucleus of a ligand ion measured from the rare-earth nucleus and \vec{r} be the position of the rare-earth electron. Also, we let \vec{r}_1 be the position of the volume element of charge $\rho(r_1) d\tau_1$ from the oxygen nucleus. Then the electric potential at the rare-earth electron at \vec{r} due to this element of charge is

$$d\phi = \frac{\rho(r_1) d\tau_1}{|\vec{R}_1 + \vec{r}_1|}, \quad (2)$$

where

⁷A. K. Raychaudhuri and D. K. Ray, *Proc. Phys. Soc.*, 90 (1967), 839.

⁸J. C. Slater, *Phys. Rev.*, 36 (1930), 57.

$$\vec{R}_1 = \vec{R} - \vec{r} \quad ,$$

$$d\tau_1 = r_1^2 dr_1 d\Omega_1 \quad ,$$

and

$$d\Omega_1 = \sin \theta_1 d\theta_1 d\phi_1 \quad .$$

Before integrating equation (2), it is convenient to expand $|\vec{R}_1 + \vec{r}_1|$ in spherical harmonics so that

$$\frac{1}{|\vec{R}_1 + \vec{r}_1|} = \sum_{\ell m} \frac{4\pi}{2\ell + 1} (-1)^\ell \left[\frac{r_1^\ell}{R_1^{\ell+1}} \right] Y_{\ell m}^* (\hat{R}_1) Y_{\ell m} (\hat{r}_1) \quad (3)$$

for $r_1 < R_1$; for $r_1 > R_1$, the factor in brackets becomes $R_1^\ell / r_1^{\ell+1}$. Since we assumed that the charge density $\rho(r_1)$ is spherically symmetric, we can integrate over $d\Omega_1$ so that

$$\int_{\Omega_1} \frac{d\Omega_1}{|\vec{R}_1 + \vec{r}_1|} = \begin{cases} \frac{4\pi}{R_1} & , \text{ for } R_1 > r_1 \quad , \\ \frac{4\pi}{r_1} & , \text{ for } R_1 < r_1 \quad , \end{cases} \quad (4)$$

where we have used the relation

$$\int_{\Omega_1} Y_{\ell m}(\hat{r}_1) d\Omega_1 = \sqrt{4\pi} \delta_{\ell 0} \delta_{m 0} \quad .$$

The electric potential at the rare-earth electron is then

$$\phi = 4\pi \int_0^{R_1} \frac{\rho(r_1)}{R_1} r_1^2 dr_1 + \int_{R_1}^{\infty} \rho(r_1) r_1 dr_1, \quad (5)$$

or

$$\phi = \frac{1}{R_1} \int_0^{\infty} 4\pi \rho(r_1) r_1^2 dr_1 - \int_{R_1}^{\infty} 4\pi r_1^2 \rho(r_1) dr_1 \left(\frac{1}{R_1} - \frac{1}{r_1} \right). \quad (6)$$

The first integral in equation (6) gives the total charge and, since $R_1 \leq r_1$, the integrand of the second integral is always positive. Thus, the potential is always less than that of a point charge located at \vec{R}_1 . If we let

$$I = \int_{R_1}^{\infty} r_1^2 \rho(r_1) dr_1 \left(\frac{1}{R_1} - \frac{1}{r_1} \right) \quad (7)$$

and use the charge distribution given in equation (1), this becomes

$$I = \frac{N4!}{\gamma^5 R_1} \left(1 + \frac{3}{4} \gamma R_1 + \frac{\gamma^2 R_1^2}{4} + \frac{\gamma^3 R_1^3}{24} \right) e^{-\gamma R_1}, \quad (8)$$

where we have used the easily derivable expression

$$\int_y^{\infty} x^n e^{-\gamma x} dx = \frac{n! e^{-\gamma y}}{\gamma^{n+1}} \sum_{v=0}^n \frac{(\gamma y)^v}{v!}.$$

Further, by differentiating $e^{-\gamma R_1}$ with respect to γ , the result on the right side of equation (8) can be written

$$\begin{aligned} & \frac{1}{R_1} \left(1 + \frac{3}{4} \gamma R_1 + \frac{\gamma^2 R_1^2}{4} + \frac{\gamma^3 R_1^3}{24} \right) e^{-\gamma R_1} \\ &= 1 - \frac{3}{4} \gamma \frac{d}{d\gamma} + \frac{\gamma^2}{4} \frac{d^2}{d\gamma^2} - \frac{\gamma^3}{24} \frac{d^3}{d\gamma^3} \frac{e^{-\gamma R_1}}{R_1} \\ &\equiv O(\gamma) \frac{e^{-\gamma R_1}}{R_1}, \end{aligned} \quad (9)$$

and equation (8) becomes

$$I = \frac{Q}{4\pi} O(\gamma) \frac{e^{-\gamma R_1}}{R_1}.$$

The entire expression of equation (6) can be written

$$\phi = Q \left(\frac{1}{R_1} - O(\gamma) \frac{e^{-\gamma R_1}}{R_1} \right), \quad (10)$$

where $R_1 = |\hat{\mathbf{R}} - \hat{\mathbf{r}}|$.

It is convenient for later work to expand equation (10) in terms of $C_{nm}(\hat{\mathbf{r}})$, defined by

$$C_{nm}(\hat{\mathbf{r}}) = \left(\frac{4\pi}{2n+1} \right)^{1/2} Y_{nm}(\hat{\mathbf{r}}),$$

so that the first term in equation (10) becomes

$$\frac{1}{|\vec{R} - \vec{r}|} = \sum_{n,m} \frac{r^n}{R^{n+1}} C_{nm}^*(\hat{R}) C_{nm}(\hat{r}) , \quad (11)$$

with $r < R$. Similarly,⁹

$$\frac{e^{-\gamma|\vec{R} - \vec{r}|}}{|\vec{R} - \vec{r}|} = \sum_{n,m} \frac{2\gamma}{\pi} (2n+1) i_n(\gamma r) k_n(\gamma R) C_{nm}^*(\hat{R}) C_{nm}(\hat{r}) , \quad (12)$$

where $R < r$ and $i_n(x)$ and $k_n(x)$ are modified spherical Bessel functions of the first and third kinds, respectively.

If we define

$$A_{nm} \equiv \frac{-eQ}{R^{n+1}} C_{nm}(\hat{R})$$

and

$$\Delta_n(r, R) \equiv \frac{R^{n+1}}{r^n} \frac{2(2n+1)}{\pi} O(\gamma) \gamma i_n(\gamma r) k_n(\gamma R) , \quad (13)$$

we can write the potential energy of the electron at r using equation (10) as

$$U(r) = -e\phi(r) \quad (14)$$

$$= \sum_{n,m} A_{nm}^* [1 - \Delta_n(r, R)] r^n C_{nm}(\hat{r}) ,$$

⁹M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards Applied Mathematics Series (1966), 445.

which shows that, if $\Delta_n(r, R)$ is positive and less than 1, the charge distribution reduces the A_{nm} that would be calculated from a point charge model. Since, as R becomes very large, $k_n(\gamma R)$ decreases as $e^{-\gamma R}$, $\Delta_n(r, R)$ vanishes, and the rare-earth electron "sees" effectively a point charge. Thus, for ions remote from the rare-earth site, a point charge model is sufficient.

3. DISCUSSION OF AND APPROXIMATIONS TO $\Delta_n(r, R)$

In defining $\Delta_n(r, R)$ by equation (13), the expression

$$O(\gamma) \left[\gamma i_n(\gamma r) k_n(\gamma R) \right]$$

occurs. With a great deal of tedious algebra using $O(\gamma)$ defined by equation (9) and using the differential equations satisfied by $i_n(x)$ and $k_n(x)$, this result is given by

$$\begin{aligned} O(\gamma) \gamma i_n(\gamma r) k_n(\gamma R) = & \frac{(2n+1)\gamma^{n+1}}{2\pi x^n} \left[F_n(x, y) i_n(x) k_n(y) \right. \\ & - G_n(x, y) i_{n-1}(x) k_n(y) + H_n(x, y) i_n(x) k_{n-1}(y) \\ & \left. - 3xy i_{n-1}(x) k_{n-1}(y) \right] , \end{aligned} \quad (15)$$

with $x = \gamma r$ and $y = \gamma R$. In this derivation, the following were used:

$$i'_n = i_{n-1} - \left(\frac{n+1}{x} \right) i_n ,$$

$$k'_n = -k_{n-1} - \left(\frac{n+1}{y}\right)k_n ,$$

and

$$z^2 w''_n + 2zw'_n - [z^2 + n(n+1)]w_n = 0 ,$$

with w_n either i_n or k_n and z given by x or y , respectively. The various functions in equation (15) are defined by

$$F_n(x,y) = \frac{(2n+3)(n+2)(2n+5)}{3} + \frac{4n+9}{6} (x^2+y^2) ,$$

$$G_n(x,y) = x \left(\frac{2n^2+11n+18}{3} + \frac{y^2}{2} + \frac{x^2}{6} \right) , \quad (16)$$

$$H_n(x,y) = y \left(\frac{2n^2+11n+18}{3} + \frac{x^2}{2} + \frac{y^2}{6} \right) .$$

The result given in equation (15), which is rigorously correct, is not very desirable. In the theory of crystal fields using the point charge model, the A_{nm} are used in conjunction with shielding factors and appropriate radial wave functions to attempt to fit the phenomenological crystal field parameters, B_{nm} , which are obtained by fitting the crystal field spectra of a given ion by using the hamiltonian

$$H = \sum_{n,m} B_{nm}^* C_{nm}(\hat{r}) . \quad (17)$$

With the inclusion of the factor $\Delta_n(x,y)$ given in the form of equation (15), this combination would be possible, but would be extremely

cumbersome. For this reason, we have chosen to replace $\Delta_n(x,y)$ by an approximation for small x (small γr).

Before proceeding, it is convenient to make a few simplifying changes in variables. We let

$$i_n(x) = \frac{2^n x^n n!}{(2n+1)!} R_n, \quad (18)$$

$$k_n(y) = \frac{\pi e^{-y}}{2y^{n+1}} \frac{(2n)!}{2^n n!} q_n,$$

where

$$R_n = 1 + \frac{x^2}{2(2n+3)} + \frac{x^4}{8(2n+3)(2n+5)} + \dots,$$

$$q_0 = 1,$$

$$q_1 = 1 + y,$$

$$q_n = q_{n-1} + \frac{y^2 q_{n-2}}{(2n-1)(2n-3)}.$$

With these changes, $\Delta_n(x,y)$ (eq 15) becomes

$$\begin{aligned}
\Delta_n(x,y) = \frac{e^{-y}}{4} & \left[F_n(x,y) q_n R_n - G_n(x,y) \frac{2n+1}{x} q_n R_{n-1} \right. \\
& + H_n(x,y) \frac{y}{2n-1} q_{n-1} R_n \\
& \left. - 3y^2 \frac{2n+1}{2n-1} q_{n-1} R_{n-1} \right] .
\end{aligned} \tag{19}$$

In this form, it is apparent from equations (16) and (19) that $\Delta_n(x,y)$ is a function of x^2 and, further, the limit $x = 0$, $y = 0$ gives $\Delta_n(0,0) = 1$. For small x , the following expansion for $\Delta_n(x,y)$ can be obtained:

$$\Delta_n(x,y) = \Delta_n(0,y) + x^2 \Delta'_n(0,y) + x^4 \Delta''_n(0,y) , \tag{20}$$

where

$$\Delta_n(0,y) = \frac{e^{-y}}{4} \left\{ \left[\frac{1}{4} + \frac{3-n}{3} y^2 \right] q_n + \frac{y^2}{3(2n-1)} \left(2n^2 - 7n + 9 + \frac{y^2}{2} \right) q_{n-1} \right\} ,$$

$$\Delta'_n(0,y) = \frac{y^2 e^{-y}}{24(2n+3)} \left\{ -nq_n + \left[n + \frac{y^2}{2(2n-1)} \right] q_{n-1} \right\} ,$$

$$\Delta''_n(0,y) = \frac{y^2 e^{-y}}{96(2n+3)(2n+5)} \left\{ -(n+3)q_n + \frac{1}{2n-1} \left[(n+1)(2n+3) + \frac{y^2}{2} \right] q_{n-1} \right\} .$$

The first term in $\Delta_n(x,y)$ from equation (20) is, in principle, only host dependent as $y = \gamma R$ and γ is dependent on the ligand ion, whereas R is the distance, which in the absence of local distortion is characteristic of the host material. The other two terms in equation (20) are dependent on the particular rare-earth ion through the factors x^2 and x^4 . From equation (14), we see that the total radial dependence of the term containing $\Delta_n(x,y)$ is of the form $r^n \Delta_n(x,y)$ and, with $x = \gamma r$, for the equivalent electrons, we can write

$$\langle r^n \Delta_n(x,y) \rangle = \langle r^n \rangle \Delta_n(0,y) + \gamma^2 \langle r^{n+2} \rangle \Delta_n'(0,y)$$

(21)

$$+ \gamma^4 \langle r^{n+4} \rangle \Delta_n''(0,y) ,$$

where $\langle r^k \rangle$ is the expectation value of r^k for the rare-earth electrons. Frequently, Hartree-Fock wave functions modified in some manner are used to calculate these expectation values. However, the unmodified Hartree-Fock functions may be sufficiently accurate to allow us to write equation (21) as

$$\langle r^n \Delta_n(x,y) \rangle = \langle r^n \rangle \left[\Delta_n(0,y) + \gamma^2 \lambda_2(n) \Delta_n'(0,y) + \gamma^4 \lambda_4(n) \Delta_n''(0,y) \right] , \quad (22)$$

where

$$\lambda_2(n) = \langle r^{n+2} \rangle / \langle r^n \rangle ,$$

$$\lambda_4(n) = \langle r^{n+4} \rangle / \langle r^n \rangle ,$$

with the $\lambda_2(n)$ and $\lambda_4(n)$ calculated once and for all for each rare-earth ion by using Hartree-Fock wave functions. The modifications of these functions could then be employed in the $\langle r^n \rangle$. The functions $\lambda_2(n)$ and $\lambda_4(n)$ were calculated for a number of rare-earth ions, and the results for Nd^{3+} and Er^{3+} are given in appendix A.

4. ESTIMATION OF γ and R

In theory, the functions $\Delta_n(0,y)$, $\Delta'_n(0,y)$, and $\Delta''_n(0,y)$ are dependent only on the host lattice through γ , which describes the size of the ligand charge distribution, and the distance, R, from the rare-earth site to the nearest ligand. It would be advantageous to have these quantities tabulated for a range of values of γ and R centered at some typical values. A rough estimate of γ for oxygen can be obtained by using the charge distribution given by equation (1) to calculate the average value of r by

$$\bar{r} = \frac{\int r \rho \, d\tau}{Q} = \frac{5}{\gamma} ,$$

and if we let \bar{r} be the ionic radius of oxygen, which is approximately 140 nm, we obtain

$$\gamma \simeq 3.57/\text{\AA} .$$

A second estimate of γ for oxygen can be obtained by using rules given by Slater⁸ for deriving the exponential factors in the wave functions for the $2p^6$ (also the $2s^2$) of oxygen to obtain a value

$$\gamma \simeq 3.86/\text{\AA} ,$$

where this value of γ is twice that given by Slater's rule since the charge distribution is proportional to the square of the wave function. To obtain an estimate of typical values of R, the x-ray data

⁸J. C. Slater, *Phys. Rev.*, 36 (1930), 57.

on a number of crystals were examined. The smallest distance found was $R \simeq 2.1 \text{ \AA}$ (the smallest Yb-O distance in YbP_3O_9), and the largest distance found was near $R = 2.6 \text{ \AA}$ (the smallest Ho-O distance in HoVO_4). A further check to find a typical range for $y = \gamma R$ was an approximate fitting of the theory to the phenomenological B_{nm} , which gave $y \sim 10$. It was then decided that the functions $\Delta_n(0,y)$, $\Delta'_n(0,y)$, and $\Delta''_n(0,y)$ should be calculated for the range of values $8 \leq y \leq 10$ (fig. 1 to 3). The results for $y = 9.6, 10$, and 10.4 are given in tabular form in appendix B. Several features of these functions are of interest. The function $\Delta_n(0,y)$ (fig. 1) always increases for larger n with y fixed, whereas the function $\Delta'_n(0,y)$ (fig. 2) is larger for intermediate n ($n \sim 4$) for small y , changing when y gets larger. The function $\Delta''_n(0,y)$ (fig. 3) is negative for some values of n for $y < 10.4$ and is positive for larger y . Each correction is of the order of 10^{-2} of the preceding term; for example,

$$\Delta'_n(0,y) \simeq \Delta_n(0,y) \times 10^{-2} .$$

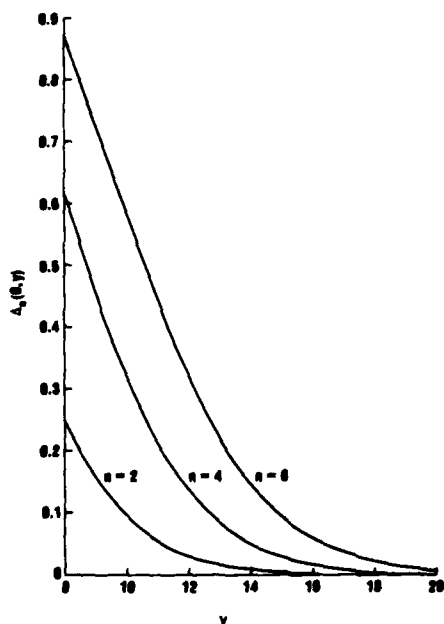


Figure 1. Function $\Delta_n(0,y)$ for $n = 2, 4$, and 6 versus y .

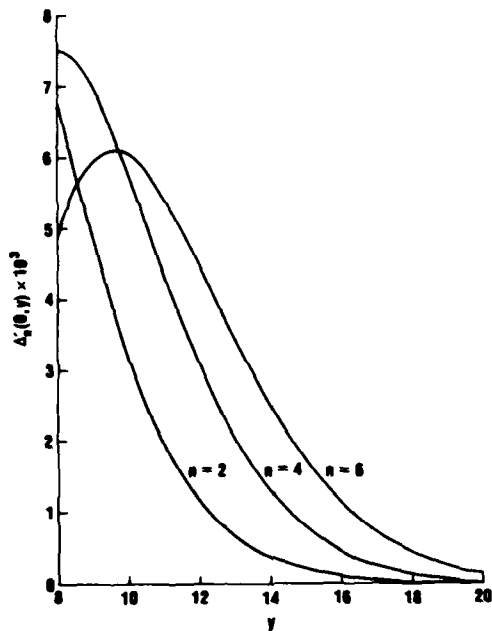
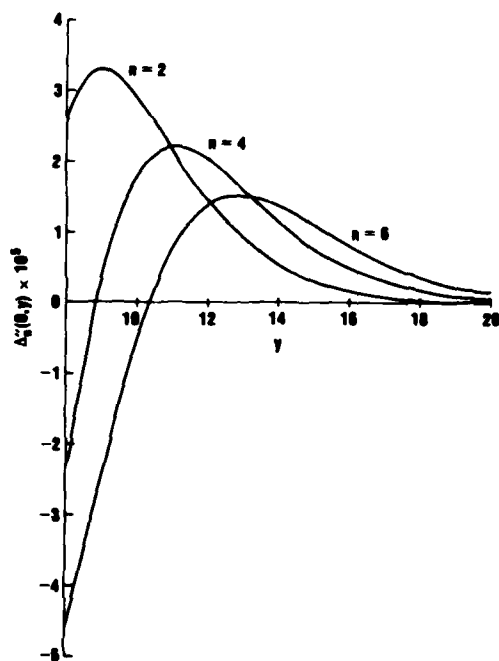


Figure 2. Function $\Delta'_n(0, y)$ for $n = 2, 4,$ and 6 versus y .

Figure 3. Function $\Delta''_n(0, y)$ for $n = 2, 4,$ and 6 versus y .



5. CONCLUSION

The theory of charge penetration by a rare-earth ion into the charge distribution on a ligand has been developed. The results are cast into a form reminiscent of the Sternheimer shielding factors, σ_n , which relate the observed $A_{nm}^{(n)} \langle r^n \rangle$ to the lattice sum $A_{nm}^{(n)} \langle r^n \rangle$ in the form

$$A_{nm}^{(n)} \langle r^n \rangle = A_{nm}^{(n)} \langle r^n \rangle (1 - \sigma_n) \quad (23)$$

The corresponding form developed here is

$$A_{nm}^{(n)} \langle r^n \rangle = A_{nm}^{(n)} \langle r^n \rangle \left[1 - \Delta_n^{(n)}(x, y) / \langle r^n \rangle \right] \quad (24)$$

with explicit expressions given for the $\Delta_n^{(n)}(x, y)$. The $\Delta_n^{(n)}(x, y)$ is then expanded for small x , and a form convenient for calculation is given.

The results obtained here can be used with the three-parameter theory of crystal fields¹ to obtain crystal field parameters $B_{nm}^{(n)}(\tau, q, \gamma)$, which give a better representation of the phenomenological $B_{nm}^{(n)}$ than we obtained previously.

¹Richard P. Leavitt, Clyde A. Morrison, and Donald E. Wortman, Rare Earth Ion-Host Crystal Interactions, 3. Three-Parameter Theory of Crystal Fields, Harry Diamond Laboratories HDL-TR-1673 (June 1975).

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APPENDIX A.--CALCULATION OF $\lambda_2(n)$ AND $\lambda_4(n)$

APPENDIX A

In equation (22) in the main body of this report, the quantities $\lambda_2(n) = \langle r^{n+2} \rangle / \langle r^n \rangle$ and $\lambda_4(n) = \langle r^{n+4} \rangle / \langle r^n \rangle$ are introduced. These quantities are given in tables A-1 and A-2 for Nd^{3+} and Er^{3+} , respectively. The Hartree-Fock wave functions of Freeman and Watson¹ are used.

TABLE A-1. VALUES OF $\lambda_2(n) = \langle r^{n+2} \rangle / \langle r^n \rangle$ AND $\lambda_4(n) = \langle r^{n+4} \rangle / \langle r^n \rangle$ FOR Nd^{3+}

n	$\lambda_2(n)$ (Å)	$\lambda_4(n)$ (Å)
0	0.28030	0.18831
1	0.43768	0.43987
2	0.67181	0.97107
3	1.00500	1.98782
4	1.44545	3.71583
5	1.97793	6.31501
6	2.57070	9.83261
7	3.19274	14.23983
8	3.82487	19.50188

TABLE A-2. VALUES OF $\lambda_2(n) = \langle r^{n+2} \rangle / \langle r^n \rangle$ AND $\lambda_4(n) = \langle r^{n+4} \rangle / \langle r^n \rangle$ FOR Er^{3+}

n	$\lambda_2(n)$ (Å)	$\lambda_4(n)$ (Å)
0	0.18652	0.08828
1	0.30141	0.21297
2	0.47331	0.46836
3	0.70659	0.91977
4	0.98955	1.60912
5	1.30171	2.54414
6	1.62611	3.71580
7	1.95446	5.11960
8	2.28508	6.76357

¹A. J. Freeman and R. E. Watson, Phys. Rev., 127 (1962), 2058.

APPENDIX B.--FUNCTIONS $\Delta_n(0,y)$, $\Delta'_n(0,y)$, AND $\Delta''_n(0,y)$

APPENDIX B

In equations (22) and (23) in the main body of this report, the functions $\Delta_n(0,y)$, $\Delta'_n(0,y)$, and $\Delta''_n(0,y)$ are introduced and depend on the spread of the wave function, γ , of the ligand and the distance, R , to the ligand through $y = \gamma R$. In the main body, it is shown that a value of $y \simeq 10$ is representative for oxide compounds. These three quantities are given for $y = 9.6$, 10.0 , and 10.4 in tables B-1, B-2, and B-3, respectively.

TABLE B-1. FUNCTIONS $\Delta_n(0,y)$, $\Delta'_n(0,y)$, AND $\Delta''_n(0,y)$ FOR $y = 9.6$

n	$\Delta_n(0,y)$	$\Delta'_n(0,y)$	$\Delta''_n(0,y)$
1	3.7795(-2)	1.8975(-3)	2.5413(-5)
2	1.1450(-1)	3.7665(-3)	3.1391(-5)
3	2.3108(-1)	5.3584(-3)	2.6028(-5)
4	3.6993(-1)	6.2777(-3)	1.3800(-5)
5	5.1102(-1)	6.4717(-3)	-5.3134(-8)
6	6.3959(-1)	6.0987(-3)	-1.1995(-5)

Note: Numbers in parentheses are powers of 10.

TABLE B-2. FUNCTIONS $\Delta_n(0,y)$, $\Delta'_n(0,y)$, AND $\Delta''_n(0,y)$ FOR $y = 10$

n	$\Delta_n(0,y)$	$\Delta'_n(0,y)$	$\Delta''_n(0,y)$
1	2.9253(-2)	1.5133(-3)	2.1619(-5)
2	9.2308(-2)	3.1528(-3)	2.9026(-5)
3	1.9320(-1)	2.7006(-5)	2.7006(-5)
4	3.1931(-1)	1.8079(-5)	1.8079(-5)
5	4.5343(-1)	6.3338(-6)	6.3338(-6)
6	5.8099(-1)	-4.9131(-6)	-4.9131(-6)

Note: Numbers in parentheses are powers of 10.

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APPENDIX B

TABLE B-3. FUNCTIONS $\Delta_n(0,y)$, $\Delta'_n(0,y)$, AND $\Delta''_n(0,y)$ FOR $y = 10.4$

n	$\Delta_n(0,y)$	$\Delta'_n(0,y)$	$\Delta''_n(0,y)$
1	2.2532(-2)	1.1981(-3)	1.8104(-5)
2	7.3957(-2)	2.6136(-3)	2.6144(-5)
3	1.6035(-1)	4.0634(-3)	2.6664(-5)
4	2.7343(-1)	2.0692(-5)	5.1755(-3)
5	3.9900(-1)	5.7737(-3)	1.1199(-5)
6	5.2339(-1)	1.0883(-6)	5.8660(-3)

Note: Numbers in parentheses are powers of 10.

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CHARGE PENETRATION EFFECTS IN RARE-EARTH CRYSTAL FIELDS.

ABSTRACT

(U) THE THEORY OF CHARGE PENETRATION BY A RARE-EARTH ION INTO THE CHARGE DIS
THE RESULTS ARE CAST INTO A FORM REMINISCENT OF THE STERNHEIMER SHIELDING FAC
A PRIME $NM \langle R \text{ TO THE } N\text{TH POWER} \rangle$ TO THE LATTICE SUM A $NM \langle R \text{ TO THE } N\text{TH POWER} \rangle$ IF
= A PRIME $NM \langle R \text{ TO THE } N\text{TH POWER} \rangle (1 - \text{SIGMA } N)$. THE CORRESPONDING FORM DEVELO
 $R \rangle = \text{A PRIME } NM \langle R \text{ TO THE } N\text{TH POWER} \rangle (1 - \text{DEKTA } N(X,Y) / \langle R \text{ TO THE } N\text{TH POWER} \rangle$
DELTA $N(X,Y)$. THE DELTA $N(X,Y)$ IS THEN EXPANDED FOR SMALL X , AND A FORM CONVE
S OBTAINED HERE CAN BE USED WITH THE THREE-PARAMETER THEORY OF CRYSTAL FIELDS
U ION GAMMA, WHICH GIVE A BETTER REPRESENTATION OF THE PHENOMENOLOGICAL BNM 1

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POWER TO THE LATTICE
USE CRYSTAL LATTICES
POWER

RARE-EARTH ION
USE IONS
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45

AUG 03, 1982

FIELDS.

EARTH ION INTO THE CHARGE DISTRIBUTION ON A LIGAND HAS BEEN DEVELOPED. THE STERNHEIMER SHIELDING FACTORS, σ_N , WHICH RELATE THE OBSERVED μ_N A μ_N TO THE N TH POWER IN THE FORM A PRIME μ_N TO THE N TH POWER > THE CORRESPONDING FORM DEVELOPED HERE IS A PRIME μ_N <R TO THE N TH POWER > A $N(X,Y)/\langle R$ TO THE N TH POWER > WITH EXPLICIT EXPRESSIONS GIVEN FOR THE FOR SMALL X , AND A FORM CONVENIENT FOR CALCULATION IS GIVEN. THE RESULT BETTER THEORY OF CRYSTAL FIELDS TO OBTAIN CRYSTAL FIELD PARAMETERS B_{NM} THAN OF THE PHENOMENOLOGICAL B_{NM} THAN WE OBTAINED PREVIOUSLY. (AUTHOR)

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